Chemical and Sr Isotope Investigations of the Lower Permian Hutchinson Salt Member of the Wellington Formation, Rice County, Kansas

by

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INTRODUCTION

Scope of the Investigation

Most existing models of evaporite deposition include solely the evaporation of normal seawater; they differ only on the mechanisms of deposition. The deposition of evaporites as a result of the progressive evaporation of seawater in a barred basin was first proposed by Ochsenius in 1877 (Hite, 1970). Raup (1970 and 1982) argued that evaporites may also be deposited as a result of the mixing of seawater brines at different stages of evaporation within a basin. On the other hand, Williams (1970) proposed that the chemical compositions of evaporite sequences may be influenced by the introduction of continental waters into seawater-dominated, evaporitic basins.

Because of the difficulty in recognizing the influence of continental waters on the deposition of evaporites, Williams' suggestion has received very little support. In determining the possible influence of an influx of continentally-derived waters on the deposition of a sequence of evaporites, chemical and isotopic data are potentially useful. Sr isotopic data may be particularly useful because of the distinct differences between the Sr isotopic compositions of marine and continental waters (Table 1). The $^{87}Sr/^{86}Sr$ ratios of continental waters differ spatially and temporally and are generally higher than that of seawater.

At any given geologic time in the history of the earth, the $^{87}Sr/^{86}Sr$ ratio of sea water was essentially uniform (Brass, 1976;

Table 1. Comparison between the $^{87}Sr/^{86}Sr$ ratios and Sr contents (in ppm) of marine and continental waters.

Source	Region	$^{87}Sr/^{86}Sr$	Sr
	Marine Waters		
Peterman et al. (1970)	Worldwide Oceans	0.7092	7
Brass (1976)	Worldwide Oceans	0.7090	7
Faure et al. (1977)	Hudson Bay	0.7093	—
	Surficial Continental Waters		
Brass (1976)	Lake Superior	0.7046	—
Jones and Faure (1972)	Bear River	0.7219	—
	Jordan River	0.7206	—
	Great Salt Lake	0.7174	—
Wadleigh et al. (1985)	Ave. Canadian Rivers	0.7110	0.084
	Subsurface Formation Waters		
Chaudhuri (1978)	Kansas (Penn)	0.7248	45
	Kansas (Miss)	0.7264	42
	Kansas (Miss)	0.7146	660

Peterman et al., 1970). This condition results because the time required for the complete mixing of the oceans' water through a single circulation (1,000 years) is rather small in comparison to the residence time of Sr in the oceans (2,000,000 years)(Veizer and Compston, 1974). However, throughout the earth's history the Sr isotopic ratio of seawater has varied randomly (Fig. 1), which may be related to the influx of Sr from sources having different Sr isotopic compositions. The major sources that influence the Sr isotopic composition of sea water are: (1) old continental silicate rocks ($^{87}Sr/^{86}Sr=0.716$), (2) young submarine volcanic rocks ($^{87}Sr/^{86}Sr=0.704$), and (3) Phanerozoic marine carbonate rocks ($^{87}Sr/^{86}Sr=0.708$) (Faure, 1977). Although homogeneity in the Sr isotopic composition of seawater may occur over a relatively short geologic time period, localized differences in the Sr isotopic composition of seawater may result when and wherever isotopically different Sr is added to the seawater. These local variations in the Sr isotopic composition of seawater may persist for a long enough time to precipitate evaporites whose isotopic compositions differ from the worldwide seawater value. Therefore, any influx of continental waters into an evaporitic basin should be evident in the Sr isotopic composition of evaporite beds, provided the continental waters had Sr isotopic compositions different enough and Sr contents large enough to affect a change in the Sr isotopic composition of the seawater in the evaporating basin. Based on this logic, Sr isotopic data appear useful in determining the role of continental waters in the precipitation of evaporites.

To determine whether Sr isotopic data are useful in detecting

the possible role of continental waters in evaporite deposition, samples from the Lower Permian Hutchinson Salt Member of the Wellington Formation were analyzed for their Sr isotopic compositions and chemical contents. The samples came from the core of the Atomic Energy Commission's Test Hole no. 1, in Rice County, Kansas. In addition to the isotopic and chemical analysis of the Hutchinson Salt evaporite sequence, interbedded shale layers were analyzed for their Pb, Cu, and Zn contents and clay mineralogy. This knowledge is potentially useful because shale beds associated with evaporite sequences have been recognized as possible source beds for many metal deposits (Thiede and Cameron, 1976).

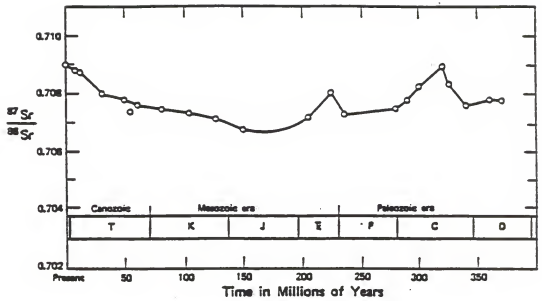


Figure 1. Systematic variation of the $^{87}Sr/^{86}Sr$ ratio of seawater during Phanerozoic time

Previous Sr Isotopic Studies of Evaporite Deposits

Clauer (1976) compared the $^{87}Sr/^{86}Sr$ ratios of Miocene evaporites with the $^{87}Sr/^{86}Sr$ ratio of contemporaneous Miocene sea water. From his work, Clauer drew the following conclusions; (1) The Sr isotopic composition of the evaporites shows a depletion in ^{87}Sr compared to Miocene marine Sr, and (2) the depletion is a result of variations in the supply of Sr from continental water and is obvious only when the influx of continental water is significant. Posey et al. (1983), however, investigated the $^{87}Sr/^{86}Sr$ ratios of Jurassic evaporites and found them similar to that of contemporaneous seawater values. Brookins and Registar (1980) analyzed Late-Permian evaporites from southeastern New Mexico and determined that the $^{87}Sr/^{86}Sr$ ratios of the halite samples ranged from 0.7071 to 0.7207. The results of these investigations indicate that only under certain circumstances can Sr isotopes be useful in determining the possible influence of the influx of continental water on the deposition of an evaporite sequence.

GEOLOGIC SETTING

Lower Permian Stratigraphy

The Permian System in Kansas has been divided stratigraphically into the Upper and Lower Permian Series. The Lower Permian Series is divided into the Gearyan and Cimarronian Stages and the Upper Permian Series contains only the Custerian Stage. The Gearyan Stage is divided into three groups, the uppermost being the Chase Group (Zeller, 1968). The Chase Group is a 300 foot-thick sequence of cherty limestone and shale beds that today form the Flint Hills of Kansas. The uppermost formation of the Chase Group is the Nolans Limestone. The Herrington Limestone Member of the Nolans Limestone represents the end of the normal marine conditions that deposited the fossiliferous limestone and shale beds of the Gearyan Stage (Swineford, 1955).

The Cimarronian Stage is divided into the lower Sumner and upper Nippewalla Groups. The rocks of the Sumner Group were deposited from brackish water (Swineford, 19550. The basal formation in the Sumner Group is the Wellington Formation (Fig 2). Zeller (19968) listed four members of the Wellington Formation which in ascending order are: (1) the Hollenberg Limestone Member, an argillaceous, dolomitic limestone one to five feet thick; (2) the Carlton Limestone, a lenticular, dolomitic, fresh water deposit containing numerous fossil insects, ranging in thickness from 5 to 25 feet; (3) the Hutchinson Salt, a dominantly halitic sequence of evaporites with many dolomite, anhydrite and shale layers ranging in thickness

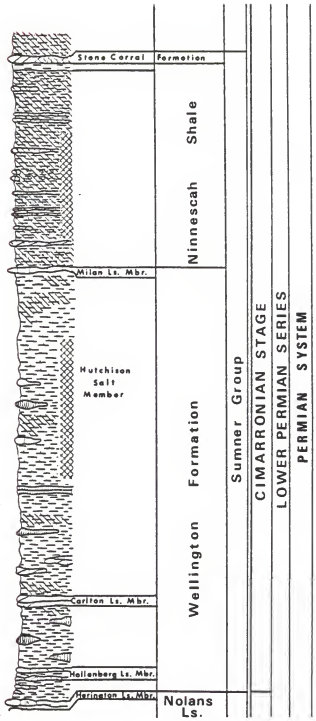


Figure 2. Stratigraphy of the Sumner Group

from greater than 600 feet in southcentral Kansas to less than one foot around the edges of the salt body; and (4) the Milan Limestone, a thin (not exceeding eight feet in thickness) unit of shaley limestone that may contain small quantities of barite (Zeller, 1968).

Above the Wellington Formation is the Ninnescah Shale, which contains red, silty shale beds with several discontinuous dolomite beds, thin sandstone layers, and evaporite deposits. The formation in approximately 300 feet thick (Swineford, 1955). The Ninnescah Shale is overlain by the Stone Corral Formation, which is a laterally persistant unit composed of beds of dolomite, anhydrite, and shale and minor amounts of salt and gypsum. The Stone Corral Formation ranges in thickness from 25 to 45 feet.

The Nippewalla Group contains many redbeds (Zeller, 1968) and is characterized by deposition in a dominantly continental environment. Thick accumulations of evaporites are found, however, within the Flowerpot and Blaine formations of the Nippewalla Group in the Syracuse Basin of western Kansas and in the Anadarko Basin of Oklahoma and Texas (Fay, 1964). The total thickness of the Nippewalla Group may exceed 1000 feet in places (Merriam, 1963, p.81).

Structure of the Hutchinson Salt

The Hutchinson Salt was deposited over most of southcentral Kansas and northcentral Oklahoma in a shallow, hypersaline arm of the early Permian sea (Hills, 1942; Tasch, 1964; Swineford,

1955)(Fig. 3). Throughout salt deposition the region sloped toward the Hugoton Embayment of the Anadarko Basin. The Hutchinson Salt basin (Jones, 1965) formed by the downwarping of the lower anhydrite beds (Swineford, 1955). This created a restricted, marine embayment that allowed for the thick accumulation of salt (Mudge, 1967). The subsidence of the basin lasted only until the end of salt deposition, as indicated by the laterally persistent thicknesses of the beds both above and below the Hutchinson Salt (Lee, 1956)(Fig. 4).

The Hutchinson Salt basin was bordered on the east by the Nemaha Anticline, which runs roughly northeast-southwest from Omaha, Nebraska to Oklahoma City, Oklahoma. The basin was bordered on the south by the Anadarko Basin and the highlands of the Wichita-Amarillo Uplift (Fig. 3). Hills (1942) noted the striking similarities between the mid-Permian Oklahoma-Kansas basin and a section found in the Delaware Basin of west Texas and New Mexico. These strongly evaporitic sequences are separated laterally by the dominantly continental Hennessey-Garber Formation of Oklahoma. Hills (1942, p. 231) stated:

> In lower (Early) Leonardian time there were two basins of saline waters joined by a narrow strait over the Wichita-Amarillo axis, but closely enough related so that they reflect nearly the same diastrophic and sedimentary changes.

The northern termination of the Hutchinson Salt is in Osborne and Rooks counties of north-central Kansas, where the salt beds gradually pinch out (Fig.4). Along the western edge of the basin is

a south-trending zone of thinning that seems to parallel the present-day axis of the Sheldon Anticline (Mudge, 1967). East of the basin the original extent of salt deposition is unknown because of the erosion of the salt bed prior to the deposition of the overlying shale beds (Dellwig, 1962). Lee (1956) and others estimated that at least half of the original salt body has been eroded and leached away.

Investigations of electric logs by Lee (1956) revealed abnormal thickening of the salt body over relatively short distances. Contrary to the expected view (i.e. that the thickening is the result of locally depressed areas), Lee stated that the anomalous thicknesses occur in anticlines, a fact he attributed to the plastic flow of evaporites during deformation. Certainly the phenomenon occurred after burial and probably after the Permian Period (Lee, 1956).

In general, faulting has not affected the Hutchinson Salt to any great extent. Microearthquake studies (Steeples, 1981) have recorded movements along the Nemaha Anticline and the Central Kansas Uplift and as such, they are mainly confined to the basement rock.

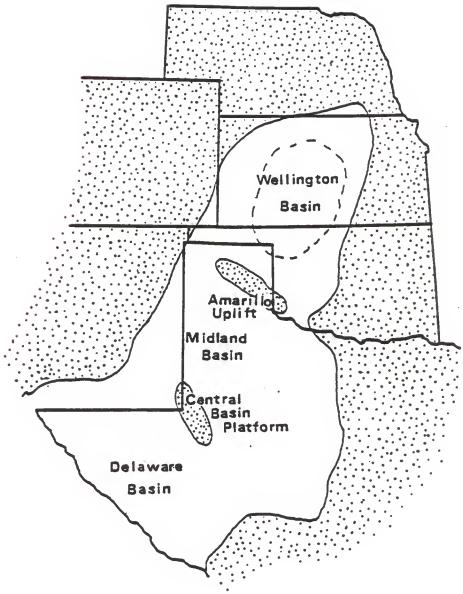
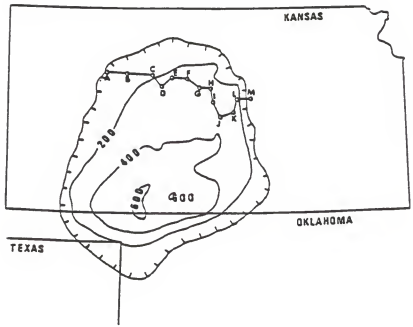


Figure 3. Paleogeographic map of the mid-continent region at the time of the deposition of the Hutchinson Salt Member of the Wellington Formation



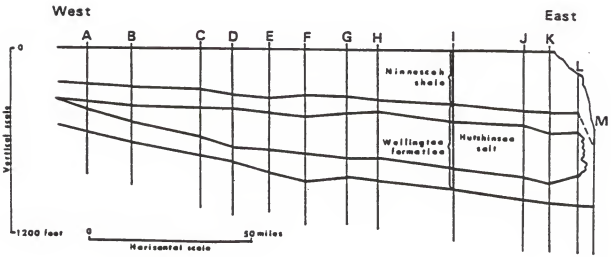


Figure 4. Present geographic extent and thickness (in feet) of the Hutchinson Salt Member of the Wellington Formation and cross-section of the Sumner Group

ANALYTICAL METHODS

Selection of Samples

The samples used in this investigation came from the core of the Atomic Energy Commision's (A.E.C.) Test Hole no. 1. This hole was drilled in 1970 to determine the feasibility of storage of nuclear wastes in the Hutchinson Salt. A.E.C. Test Hole no. 1 is in Section 26, Township 18 south, Range 8 west, Rice County, Kansas. The core is presently stored at the Kansas Geological Survey.

Samples were taken at several points along the core in an attempt to represent a comprehensive vertical sequence. Twenty-three samples (9halite, 6 anhydrite, 3 dolomite, and 5 shale samples) representing the different phases of the evaporite sequence were analyzed from the 400 foot evaporitic section of the core (Fig. 5).

Preparation of Samples

Distilled and demineralized water was used in washing. Hydrochloric (HC1) and nitric (HNO_3) acids used in dissolutions and column separations were distilled in a vycor-glass, acid-distilling apparatus. A commercial grade perchloric ($HC1O_4$) acid was used in anhydrite and shale dissolutions. Prior to use, all laboratory wares were washed in soap and water, soaked in 2N HCl for at least one hour, and thoroughly rinsed in distilled and demineralized water.

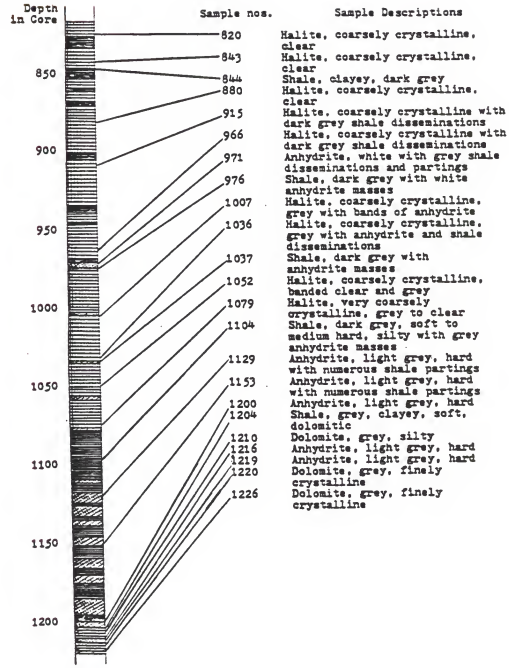

Depth in Core
Sample nos.
Sample Descriptions
850
900
950
1000
1050
1100
1150
1200
820 Halite, coarsely crystalline, clear
843 Halite, coarsely crystalline, clear
844 Shale, clayey, dark grey
880 Halite, coarsely crystalline, clear
915 Halite, coarsely crystalline with dark grey shale disseminations
966 Halite, coarsely crystalline with dark grey shale disseminations
971 Anhydrite, white with grey shale disseminations and partings
976 Shale, dark grey with white anhydrite masses
1007 Halite, coarsely crystalline, grey with bands of anhydrite
1036 Halite, coarsely crystalline, grey with anhydrite and shale disseminations
1037 Shale, dark grey with anhydrite masses
1052 Halite, coarsely crystalline, banded clear and grey
1079 Halite, very coarsely crystalline, grey to clear
1104 Shale, dark grey, soft to medium hard, silty with grey anhydrite masses
1129 Anhydrite, light grey, hard with numerous shale partings
1153 Anhydrite, light grey, hard with numerous shale partings
1200 Anhydrite, light grey, hard
1204 Shale, grey, clayey, soft, dolomitic
1210 Dolomite, grey, silty
1216 Anhydrite, light grey, hard
1219 Anhydrite, light grey, hard
1220 Dolomite, grey, finely crystalline
1226 Dolomite, grey, finely crystalline

Figure 5. Lithology and location of core samples from the Hutchinson Salt Member of the Wellington Formation

All samples of evaporite were broken into pebble-sized pieces and the pebbles were then examined under a binocular microscope. All pebbles containing clastic veins or disseminations were rejected. The remaining samples were crushed into a fine powder using a clean, agate mortar and pestle. The powder was transferred to pre-cleaned plastic bottles for storage.

The five shale samples used in clay mineral analyses were crushed in a clean mortar and pestle and dry-sieved through a 200 mesh sieve. The smaller size fraction was collected while the larger size fraction was sieved a second time. The less than 200 mesh sieved material was then placed in a Waring blender with approximately 1 liter of distilled water and blended for 10 to 15 minutes. The slurry was transferred to a clean glass beaker and allowed to settle for approximately 48 hours. Because of large amounts of salts in the shale samples, repetition of the washing process was necessary. An antifloculant (1M sodium hexametaphosphate) was added during the washing process to insure complete separation of the clay particles and removal of all salts.

The less than 2 u and less than 0.5 u size fractions were separated from the raw sample of centrifuging. Oriented slides were prepared from the slurries by placing several drops of the slurry on a glass slide and air-drying.

Ethylene glycol was used to distinguish the expandable 2:1 clay minerals, such as smectite or vermiculite, from the non-expandable clay minerals. This organic liquid enters the interlayer sites of expandable minerals causing growth of the unit cell along the c-axis. To obtain the effect, untreated slides were placed in a

desiccator containing the ethylene glycol and allowed to sit for 24 hours. The slides were analyzed immediately after removal from the desiccator.

Heating the oriented slides (usually after glycolation) to 450 C and 600 C was done in a Lindberg oven. The slides were placed in the pre-heated oven for at least one hour and analyzed immediately after removal to minimize the effect of rapid rehydration. Heat treatments aided in distinguishing kaolinite, which decomposes at about 550 C, and the expandible clays minerals, which lose their structural water at various temperatures.

In order to distinguish kaolinite peaks from other 7 A reflections (i.e. d(200) chlorite and d(004) mixed layer), an oriented slide was placed in a desiccator containing hydrazinium hydroxide. The slides were left in the desiccator for 24 hours to allow for complete saturation of the slide with the vapor. The slides were analyzed immediately after removal from the desiccator.

Preparation of Stock Solutions

The nine halite stock solutions were prepared by dissolving approximately 15 g of raw salt in less than 50 ml of distilled and demineralized water. The insoluble residue was filtered out, air-dried, weighed, and the exact sample weight calculated. The solution volume was then adjusted to exactly 50 ml using a volumetric flask.

The six anhydrite samples were dissolved by placing approximately 0.5 g of crushed sample in approximately 15 ml of

perchloric acid, and then evaporated to dryness. The remaining material was redissolved in approximately 20 ml of 2N HCl, and filtered, and the volume was adjusted to exactly 25 ml using distilled and demineralized water. The residue was dried, and weighed, and the exact amount of dissolved anhydrite in the 25 ml solution was calculated.

In two of the dolomitic samples (no. 1210 and no. 1226), approximately 0.7 g of crushed sample was dissolved in approximately 50 ml of 2N HCl, and the final solution volume was adjusted as in the halitic samples. Sample no. 1220 was dissolved by the same procedure using 0.95 g of crushed sample and approximately 65 ml of 2N HCl. The final volume was adjusted to 75 ml.

Stock solutions of Pb, Cu, and Zn used in the analysis of shale samples from the Hutchinson Salt were prepared in the following manner. A small amount of shale sample was placed in a clean, agate mortar and pestle and crushed into a fine powder. The samples were washed in distilled-demineralized water to remove any evaporitic minerals, filtered, and air dried. A known quantity of each washed sample was dissolved in a small amount of hydrofluoric acid (HF) and evaporated to dryness. The residue was redissolved in a small volume of concentrated HCl and the total volume of the solution was adjusted to exactly 25 ml by adding distilled-demineralized water.

Instrumental Analysis

Atomic Absorption--Determination of Ca, Mg, K and Li concentrations in the 18 evaporite samples was done by atomic absorption

spectrophotometry on a Perkin-Elmer model 305B spectrophotometer. The elemental concentrations were determined by comparison with standards of known concentration. The values were checked by analyzing one or two of the samples by the method of standard additions because of the extremely high concentrations of Ca or Na in the evaporite samples. This method involved the addition of a measured amount of a standard-elemental solution to a set volume of sample solution. This spiked solution along with an unspiked or pure sample solution was then analyzed by atomic absorption spectrophotometry. For greater accuracy, variable concentrations of the elemental spike solution were added and analyzed. The absorption readings for all of the spiked and unspiked solutions were plotted on a graph and the elemental concentration of the sample solution was calculated.

At least three standard solutions were prepared for each element analyzed by atomic absorption spectrophotometry. The concentrations of these standards differed depending on the linear range for the element. A background matrix was placed in each standard to minimize the effect of background interference (i.e. the combined effects of ionization in the flame, molecular absorption, and light scattering). The composition of the background matrix differed for different elements. La was added in most cases to both the standard and the sample solutions to minimize the effects of complexing. Na or Ca was added to the standards in some cases to eliminate the effects of ionization in the flame. A blank solution containing only the background matrix in demineralized water was analyzed along with the standards.

The Cu and Zn concentrations of the halite samples and the Cu, Zn and Pb concentrations of the shale samples from the Hutchinson Salt were determined by Atomic absorption spectrophotometry. The method of standard additions was used to minimize the effect of the background matrix in the samples.

Determination of Chloride--The chloride concentrations of the halite samples were obtained using a Bucher Digital Chloridometer. The method of analysis involves the coulometric generation of Ag ions at a constant rate. The titration end point is indicated by a sharp rise in concentration of the Ag ion when all of the C1 is exhausted. The C1 concentration is proportional to the elapsed electrolysis time. The error for the C1 concentrations is approximately 3 percent.

Determination of Sulfate--The SO_4 contents of the nine halite samples were determined by the Turbidity-Null method using a Coleman Model 14 Universal Spectrometer. In this method, 50 ml of standard SO solution and the halite sample solutions were mixed with 10 ml of salt-acid-glycerol solution. The addition of 0.3 grams of 30-40 mesh BaCl crystals causes SO_4 to complex with BaCl and precipitate as $BaSO_4$. This solution was then poured into square cuvets and the percent transmittance (T) was determined. The SO_4 concentration of the sample is inversely related to the percent transmittance. The error in the SO_4 values is approximately 2 percent.

Mass Spectrometry--Sr was separated from all other cations using a

cation exchange resin. Stock solutions of dissolved halite, anhydrite, and dolomite were placed in Teflon beakers and evaporated to dryness. The amount of stock solution necessary to obtain the required 30 to 40 ug of Sr varied with the Sr concentration of the solutions. The salts remaining after evaporation were redissolved in 3 ml of 2N HCl and carefully loaded into the resin and columns. The columns were then eluted with a predetermined amount of 2N HCl and the Sr collected at the appropriate time. Because of the extremely high Na contents in the halite samples, it was necessary to use two sets of columns in order to ensure complete and total Sr eparation. The solution containing the final collection of Sr was evaporated to dryness and redissolved in 2N HNO3. The solution was transferred to glass microbeakers, evaporated, and then heated to oxidize any organic residue.

The Sr concentrations of the evaporite samples were determined by isotope dilution. Approximately 10 ug (1 to 2 ml of stock solution) of Sr was placed in a Teflon beaker and mixed with 1 ml of a Sr spike solution of known isotope composition. The solutions were then evaporated to dryness, redissolved in 3 ml of 2N HCl, and placed in the ion-exchange columns. The Sr was separated and collected as previously explained. In determining the Rb concentrations a similar procedure was followed using 1 ml of a Rb spike solution and approximately 15 ug of Rb.

Mass spectrometric analyses were performed on a 6-inch radius, 60-degree sector, Nier-type spectrometer (Nuclide Corporation Model 6-60S). The nitrated sample of Sr or Rb was evaporated onto a clean, tantalum filament and placed into the source of the

spectrometer. The sample was degassed for five to ten minutes prior to analysis. Measurements were taken by reading peak heights on a strip-chart recorder. All values were standardized to the $^{86}Sr/^{88}Sr$ ratio of 0.1194.

X-ray Diffraction--X-ray diffraction patterns were obtained for clay mineral samples as well as for anhydrite and dolomite samples. The identification of these minerals was done using a Norelco Wide-Range diffractometer. Oriented slides of the clay mineral samples were scanned from 0 to 30 degrees 2-theta with Ni filtered Cu K-alpha radiation. The scanning speed was 30 inches per hour. Randomly oriented slides of the anhydrite and dolomite samples were scanned from 0 to 40 degrees 2-theta.

RESULTS

Elemental Abundances

The cation concentrations of K, Li, Rb, Ca, Mg and Sr were determined for the halite, anhydrite and dolomite samples. Anion concentrations of Br, Cl and So were measured in all the halite samples. The results of the analyses are in Table 2.

Halite Samples--The variations in the K (45 to 195 ppm, Mg (43 to 531 ppm), an Sr (22 to 51 ppm) concentrations of the halite samples as a function of depth in the core are in Figure 6. The highest concentrations of K and Mg occur in samples no. 880. The lowest concentrations of these elements are in sample no. 1052. All values obtained for the K, Mg, and Sr concentrations in the Hutchinson Salt compare favorably with values from analyses of similar evaporitic sequences (e.g. Dean and Tung, 1974).

The Ca concentrations of the halite samples ranged from 12 ppm to 2988 ppm. The Rb contents of the halite samples ranged from 0.02 to 0.22 ppm, whereas Li contents ranged between 1.37 to 1.80 ppm.

The data in Figure 7 show the variation in the Br, Cl, and SO_4 concentrations of the halite samples. The values are generally within the expected range for predominantly marine halitic rocks. The lowest Br concentration of the analyzed samples was 46 ppm in sample no. 820 and the highest Br content was in sample no. 880. The Cl contents ranged from 53 percent in sample no. 843 to 60 percent in sample no. 1036 and the SO_4 concentrations ranged from

Table 2. Major-and trace- element concentrations (in ppm) in evaporite samples from the Hutchinson Salt Member of the Wellington Formation.

Sample no.*	Ca	Mg	Sr	K	Rb	Li
			Halite Samples			
820	12	156	38	52	—	1.41
843	2730	209	49	77	—	1.59
880	1533	531	27	195	0.22	1.61
915	173	65	51	60	—	1.37
966	1044	125	41	63	—	1.37
1007	1854	113	39	73	—	1.72
1036	2989	156	43	60	0.02	1.80
1052	1813	43	40	45	0.22	1.57
1079	108	202	22	99	—	1.49
			Anhydrite Samples			
971	256120	2859	2552	160	3.33	3.09
1129	412500	32100	3842	730	10.92	—
1153	428350	469	3329	169	3.58	4.68
1200	257350	314	1638	118	2.24	7.98
1216	499990	—	2852	90	2.60	4.69
1219	521740	—	3080	163	1.18	4.89
			Dolomite Samples			
1210	168410	52400	2718	639	2.70	17.40
1220	159510	124060	378	1233	5.26	29.90
1226	196080	134080	535	437	5.79	32.00

Sample no.*	Cl	Br	SO_4
	Halite Samples		
820	580510	46	418
843	531740	60	3830
880	578510	100	3755
915	570970	78	645
966	534780	87	2785
1007	581990	50	3646
1036	598060	64	4529
1052	582600	60	3919
1079	576340	52	416

* Sample numbers correspond to depth in the core

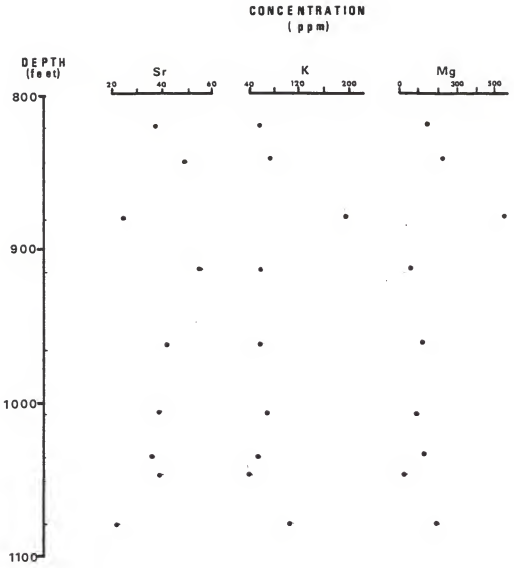


Figure 6. Variations in the Sr, K, and Mg concentrations of halite samples from the Hutchinson Salt Member of the Wellington Formation

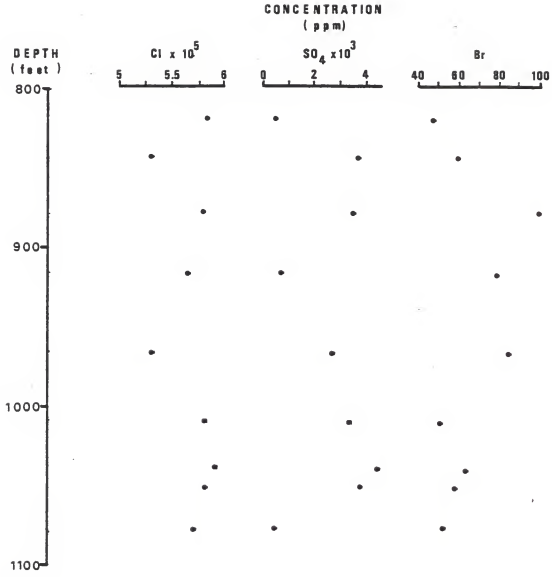


Figure 7. Variations in the Cl, SO_4, and Br concentrations of halite samples from the Hutchinson Salt Member of the Wellington Formation

416 ppm in sample no. 1079 to 4529 ppm in sample no. 1036. Sample no. 1036 also had a correspondingly high Ca concentration of 2989 ppm. These high values may be related to an anhydrite bed immediately below sample no. 1036.

Anhydrite Samples--The variations in the amounts of Ca (26 percent of 52 percent), Sr (1638 to 3842 ppm), and Mg (314 to 32,100 ppm) in the anhydrite samples generally reflect the relative proportions of dolomite incorporated in the samples. Sample no. 1129 has the highest Mg concentration (32,100 ppm) and is a mixture of dolomite and anhydrite. The lowest Mg concentrations (314 to 469 ppm) are found in the relatively pure anhydrite samples (nos. 1153 and 1200).

Ca concentrations in the anhydrite samples ranged from 26 percent in sample no. 971 to 52 percent in sample no. 1219. The low value of sample no. 971 can be attributed to inclusions of halite in the sample. The Sr contents of the anhydrite samples ranged from 1638 ppm in sample no. 1200 to 3329 ppm in sample no. 1129.

Except for sample no. 1129, the Rb and K contents for all other samples were between 1.2 and 3.6 ppm and 90 and 169 ppm respectively. Sample no. 1129 had a Rb content of 10.9 ppm and K content of 730 ppm the high values of which can be partly attributed to the presence of some dolomite in the sample. Li concentrations of the anhydrite samples ranged from 3.1 ppm to 8.0 ppm.

Dolomite Samples--As in the anhydrite samples the Ca/Mg ratios of the dolostones reflect the mineralogic mixing that has taken place. The lowest ratio (1.27) is in the purest dolomite, sample no.1220.

Based on Chillingar's (1957) classification, sample no. 1220 is a Mg dolomite. Sample no9s. 1210 and 1226 are mixtures of dolomite and anhydrite and cannot be accurately classified by atomic absorption. The Sr concentration of the pure dolomite sample no. 1220 was 378 ppm, whereas that of sample nos. 1210 and 1226 were 2718 and 535 ppm respectively.

The K concentration of the pure dolomite sample was similar to those of other dolomite samples that occur with evaporites. Sample no. 1220 contained a fairly low Rb concentration (5.26 ppm) but a higher Li concentration (29.9 ppm) indicating that this dolomite sample is enriched in Li 1.5 to 2.0 times relative to other dolomite samples associated with evaporites.

Sr-Isotopic Abundances

The measured $^{87}Sr/^{86}Sr$ ratios were obtained for six halite, six anhydrite, and three dolomite samples. These measured values are the present-day ratios. The initial ratios were obtained by making appropriate corrections for the radiogenic growth of ^{87}Sr in the samples since the Late Permian Period. The initial ratios and the Sr and Rb concentrations and Rb/Sr ratios of all evaporite samples analyzed for their Sr isotopic composition are in Table 3.

The initial $^{87}Sr/^{86}Sr$ ratios of the halite samples ranged between 0.70848 and 0.70897, whereas the initial ratios of the five pure anhydrite samples ranged from 0.70815 to 0.70845. Anhydrite sample no. 971, which contains appreciable amounts of halite, and an $^{87}Sr/^{86}Sr$ ratio of 0.70885. The $^{87}Sr/^{86}Sr$ ratios of the dolomite

samples ranged for 0.70840 to0.70879. The pure dolomite sample no 1220 had a ratio of 0.70879. The two other dolomite samples, no. 1226 and no. 1210, contained some anhydrite and their ratios were 0.70846 and 0.70840. All samples analyzed had $^{87}Sr/^{86}Sr$ ratios greater than the value of 0.70750 given by Peterman et al. (1970) for contemporaneous sea water. Figures 8a, 8b, and 8c are plots of the $^{87}Sr/^{86}Sr$ ratios against the 1/Sr values for all of the samples and the data are highly scattered.

Table 3. Sr--isotope chemistry of evaporite samples from the Hutchinson Salt Member of the Wellington Formation (concentrations in ppm).

Sample	Rb	Sr	Rb/Sr	$(^{87}Sr/^{86}Sr)$
		Halite Samples		
843	< 0.1	48.7	0.002	0.70858
880	0.22	26.5	0.008	0.70897
915	< 0.1	51.1	0.002	0.70881
966	< 0.1	41.3	0.002	0.70850
1036	0.02	42.8	0.001	0.70882
1052	0.22	39.8	0.006	0.70848
		Anhydrite Samples		
971	3.33	2551	0.001	0.70885
1129	10.92	3842	0.002	0.70845
1153	3.58	3329	0.001	0.70830
1200	2.24	1638	0.001	0.70815
1216	2.60	2853	0.001	0.70830
1219	1.18	3080	< 0.001	0.70822
		Dolomite Samples		
1210	2.70	2718	0.001	0.70840
1220	5.26	378	0.014	0.70879
1226	5.79	535	0.012	0.70846

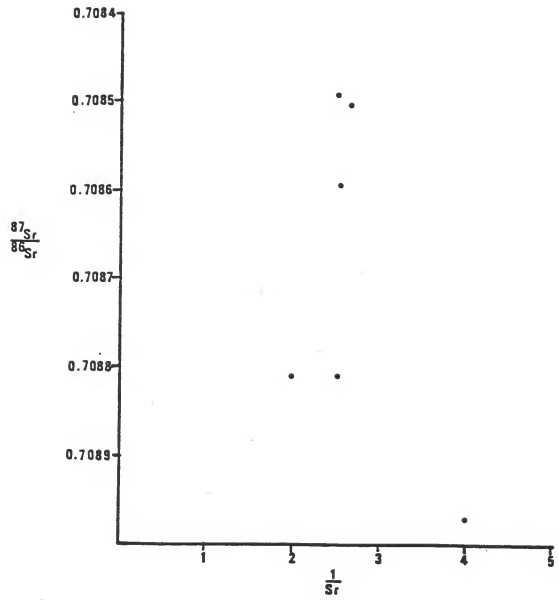


Figure 8a. Plot of the $^{87}Sr/^{86}Sr$ ratios vs. the 1/Sr values of halite samples from the Hutchinson Salt Member of the Wellington Formation

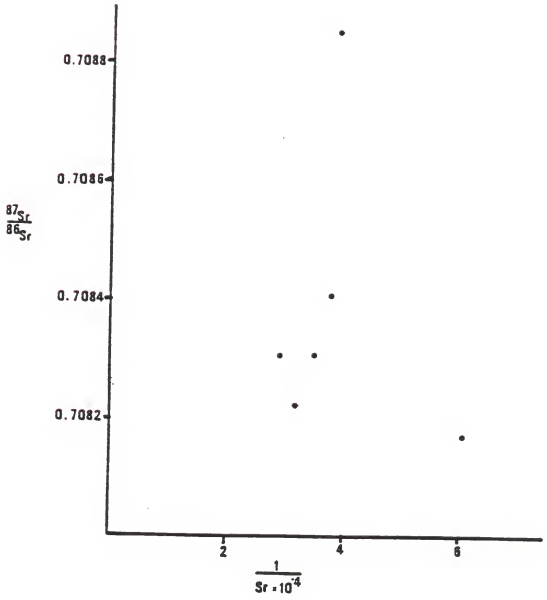


Figure 8b. Plot of the $^{87}Sr/^{86}Sr$ ratios vs. the 1/Sr values of anhydrite samples from the Hutchinson Salt Member of the Wellington Formation

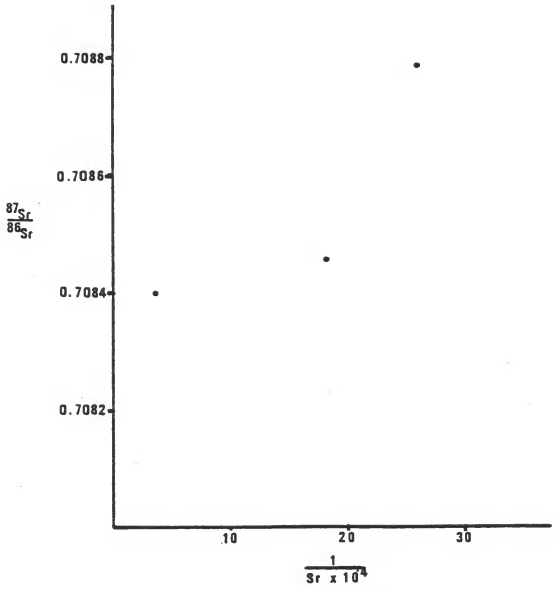


Figure 8c. Plot of the $^{87}Sr/^{86}Sr$ ratios vs. the 1/Sr values of dolomite samples from the Hutchinson Salt Member of the Wellington Formation

X-ray Diffraction of Anhydrite and Dolomite

All samples of anhydrite and dolomite were analyzed by powder diffraction to determine their mineralogic components. The results of these analyses are in Figure 9. The most useful data derived from powder diffraction were that large amounts of anhydrite occurred in the dolomite samples (nos. 1212 and 1226), halite occurred in the anhydrite sample no. 971, and dolomite occurred in anhydrite sample no. 1129. Furthermore, all anhydrite samples (except sample no. 971) contained traces of gypsum and halite.

Pb-Cu-Zn Analysis

Shale Layers.--The Pb concentrations of the shale samples ranged from 4.6 to 14.2 ppm, the Cu concentrations from 22.9 to 854.8 ppm, and the Zn concentrations from 172.0 to 1709.4 ppm. The metal contents of all shale and halite samples analyzed are in Table 4. The highest concentrations of all three metals were found in shale sample no. 1204. This shale bed is within the anhydrite section of the evaporite sequence and is approximately 120 feet below the lowest halite zone in the core. The lowest concentrations of metals in the shale beds were found in sample no. 1104, which is approximately 20 feet below the base of the halite zone and is part of the thickest shale zone sampled.

Halite Layers.--The Zn concentrations of the halite samples (ranging from 2.3 to 9.0 ppm) were generally 10 times the Cu concentrations

(ranging from 0.14 to 0.54 ppm) except for samples nos. 1052 and 880 whose Zn concentrations were 5 times their Cu concentrations. The highest Cu concentration within the halite samples was in sample no. 843. This sample also contained the second highest Zn concentration exceeded only by the value of 9 ppm in sample no. 966. The lowest Zn concentration was in the stratigraphically lowest halite sample (no. 1079) whereas the lowest Cu concentration was in the stratigraphically highest halite sample (no. 820).

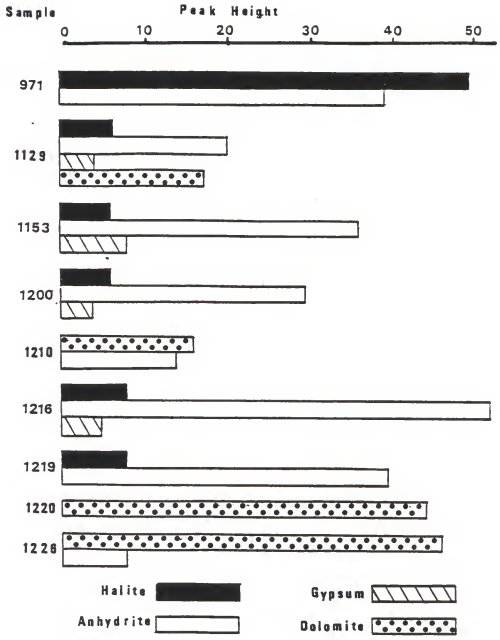


Figure 9. Minerologic composition of evaporite samples from the Hutchinson Salt Member of the Wellington Formation as determine by powder diffraction

Table 4. Metal contents (in ppm) of halite and shale samples from the Hutchinson Salt Member of the Wellington Formation.

Sample	Lithology	Pb	Cu	Zn
820	halite	____	0.10	2.50
843	halite	____	0.50	6.30
844	black shale	4.60	47.70	286.30
880	halite	____	0.50	2.40
915	halite	____	0.10	2.90
966	halite	____	0.20	9.00
976	black shale	6.00	381.50	361.00
1007	halite	____	0.20	4.70
1036	halite	____	0.20	4.40
1037	black shale	5.70	416.50	796.60
1052	halite	____	0.40	2.80
1079	halite	____	0.20	2.30
1104	black shale	____	22.90	172.00
1204	black shale	14.20	854.80	1709.40

Clay Mineralogy

The clay minerals in all shale samples from the Hutchinson Salt were illite, chlorite, and a mixed layer clay mineral thought to be corrensite. Both the < 2 um and < 0.5 um size fractions were analyzed; however, no major mineralogic differences were evident between the two size fractions. The relative abundance of illite in the shale samples ranged from 65 percent in sample no. 1204 to 45 percent in sample no. 1037. The relative abundance of corrensite ranged from 50 percent in sample no. 1037 to 30 percent in sample nos. 1104 and 1204, whereas that of chlorite was between 5 percent and 10 percent in all shale samples (Table 5). No relationship was evident between the clay mineralogy of the shale samples and their location in the evaporite sequence. The basic criteria for the identification of clay minerals is discussed.

Illite.--Illite was identified by a persistent series of basal reflections at 10 A, 5 A, and 3.3 A (Fig. 10). The locations of these peaks were not altered by either glycol or heat treatments, however, the shape of the peaks was altered by hear treatments. A slight tail to the low angle side of the illite 10 A and 5 A peaks was evident on the untreated runs and the absence of this tail after heating results in the peaks' increased sharpness. The disappearance of the tail can be related to the dehydration of any poorly crystalline illite in the untreated sample (Thorez, 1976).

Table 5. Relative abundance of clay minerals in shale samples from the Hutchinson Salt Member of the Wellington Formation.

Sample no.	Percent Illite	Percent Chlorite	Percent Corrensite
844	50	10	40
976	60	5	35
1037	45	5	50
1104	60	10	30
1204	65	5	30

The maximum intensity and sharpness of all the illite peaks occurred after heating to 450 C. Further heating decreased the intensity without affecting the sharpness of the peaks.

Chlorite.--Chlorite was determined by the uniform occurrence of the d(001) reflection at approximately 14 A throughout glycol, heat, and hydrazined treatments. The d(001), 14 A chlorite peak was hidden by the d(002) mixed-layer peak in the untreated samples; however, heat treatments collapsed basal spacing of the mixed-layer lattice to 24 A and the d(001) mixed-layer peak appeared at 12 A exposing a moderately strong 14 A chlorite peak. The appearance of the d(001) chlorite peak after heating may not be simply the result of a shift in the d(002) mixed-layer peak because the 14 A chlorite peak was not exposed when the mixed-layer d(002) peak shifted to 15.5 A after glycolation. Grim (1968) stated that in the temperature range of 400 C to 700 C the d(001) chlorite peak becomes more intense while the d(002) and d(003) peaks decrease in intensity. In these samples a definite decrease in the intensity of the 7.15 A, d(002) chlorite peak was observed after heat treatments.

Hydrazene treatments were performed on the samples to check for the presence of kaolinite. After treatment with hydrazine, the d(001) Kaolinite peak shifts from 7.15 A to 10.4 A. Because no change, either in the intensity or in the displacing of the 7.15 A peak was evident after the hydrazene treatment, kaolinite was considered to be absent from the samples.

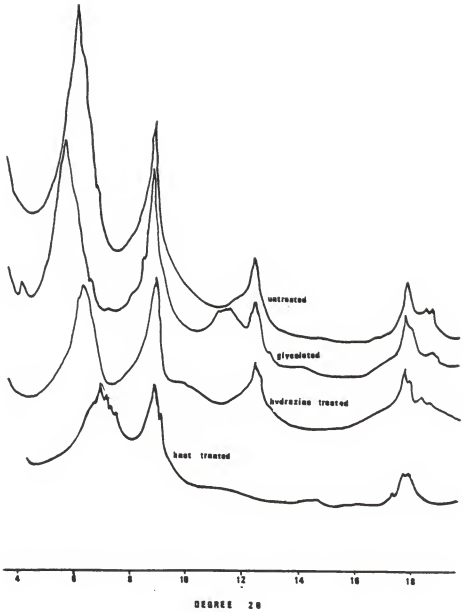


Figure 10. X-ray diffraction patterns of shale samples from the Hutchinson Salt Member of the Wellington Formation

Mixed-Layer Clay Mineral.--Identification of the mixed layer clay was done through observation of peak shifts after glycolation and heat treatments. Diffractograms of all untreated shale samples show a series of basal reflections at 14.3 A, 7.15 A, 4.75 A, and 3.55 A indicative of a 2:1 structural type of clay mineral, such as a smectite or chlorite. However, glycolation increased the 14.3 A peak to 15.6 A and heat treatment decreased the peak to 12 A. Interstratification is proposed to explain these peak shifts.

Grim (1968) described two types of interstratification, regular and random. The main criterion for the designation of regular interstratification is an integral series of basal reflections (McEwan, Ruiz-Ali, and Brown, 1961). Most reflections in these samples appeared integral or nearly so; however, several non-integral reflections were present. Thus, the mixed-layer clays in the shale samples from the Hutchinson Salt are almost regularly interstratified structures (Thorez, 1976). The peak at 14.3 A in the untreated samples indicates that any two component mixing must involve two 14 A minerals (creating a 28 A structure according to the form d(001)a + d(001)b = d(001)ab). The shift of this 14.3 A peak (i.e. the d(002) mixed-layer) to 15.6 A after glycolation indicates that one component is nonexpandable. Similarly, in the hear treatments, the swelling component dehydrates from 14 A to approximately 10 A resulting in a 24 A lattice (14 A + 10 A = 24 A) and a d(002) of approximately 12 A. Because it is necessary for one component to remain at 14 A throughout the treatments, a chlorite-expandable clay mixed-layering is suggested. Because the

expandable component dehydrates 10 A after heat treatment, swelling chlorite can be disregarded. Whether the expandable component is vermiculite or smectite could not be determined without further treatments.

The only d(001) mixed-layer peaks were observed in the heated runs at 21 A to 23 A, which is somewhat lower than the expected range of the d(001) reflection calculated from the lower basal reflections (i.e. after heat treatments, if the d(002) is found at 12 A the d(001) should be at 24 A). A similar situation was observed by Earley et al. (1956) in a regularly interstratified chlorite-montmorillonite, and by Bradley and Weaver (1956) in a regularly interstratified chlorite-vermiculite (Table 6). The former authors stated that the mixed-layer clay may be behaving in a manner similar to that of chlorite, showing modified basal intensities after heat treatments in the 500 C to 700 C range.

Table 6. Comparison of several interstratified clay minerals.

d(001)	untreated	glycolated	heated
	Sample 1204		
001	____	____	22.41
002	14.30	15.55	12.30
003	9.11	*	____
004	7.10	7.73	____
005	____	____	4.89
006	4.76	*	____
	Sample 1037		
001	____	____	20.92
002	14.30	15.49	11.87
003	*	*	____
004	7.13	7.81	____
005	____	6.24	4.90
006	4.81	*	____
	Earley et al. (1956)		
001	30.50	32.00	21.30
002	14.50	16.10	11.80
003	9.70	9.90	8.00
004	7.25	8.01	____
005	____	____	4.87
006	4.85	5.34	____
	Bradley and Weaver (1956)		
001	29.00	31.00	23.00
002	14.60	15.50	12.00
003	9.70	10.20	8.00
004	7.30	7.70	6.00
005	5.90	6.20	4.77
006	4.90	5.12	4.00

____ peak absent
* peak hidden

DISCUSSION OF CHEMICAL DATA

Halite Samples

Chemical data can reveal the depositional or diagenetic history of evaporite deposits. Br contents of salt beds are often good tracers for the recognition of d iagenetic recrystalllization of the salt beds. Valyasko (1956) reported that primary halite precipitated from evaporated seawater has Br concentrations between 50 and 60 ppm; however, experimental data on the distribution coefficient of Br in halite indicate that a minimum value of 75 ppm is characteristic of halite precipitated from evaporated seawater (Holser, 1965). In this study, the Br contents of the halite samples ranged from 46 to 100 ppm; therefore, according to Valyasko's (1956) standards, all but one (no. 843) of the halite samples reflect precipitation from evaporated seawater brines. The highest Br content is in sample no. 880, which also had the highest K and Mg contents. The high concentrations of Br, K, and Mg in sample no. 880 indicate a higher salinity of the brine in the Hutchinson Salt basin during precipitation (Dean and Tung, 1974). The low value of the stratigraphically lowest halite sample (52 ppm in sample no. 1079) is almost equal to the value predicted by Valyasko (1956) for the beginning stages of halite crystallization. The next lowest sample in the core (no. 1052) had the lowest K and Mg values of the halite samples and a Br content of 60 ppm. The gradual overall increase of Br concentration in stratigraphically higher halite samples may represent the progressive concentration of

the evaporating seawater brine. The irregular increases could be attributed to periodic influxes of continental and ocean waters into the evaporating basin (Holser, 1965).

Table 7 is a list of the Mg/Cl, Br/Cl, Ca/Cl, and SO_4/Cl ratios of the salt samples from this investigation and of brine inclusions in the Hutchinson Salt analyzed by Holser (1962). The data indicate that while the Hutchinson Salt samples consist predominantly of halite, the fluid inclusions have reached a much greater stage of concentration than halite-saturated brines (indicated by the higher Mg, Ca, and Br values).

The K/Na, Ca/Na, and Br/Cl ratios of the brines from which the halite precipitated were calculated using experimentally derived distribution coefficients given by Holser (1979). The distribution coefficients of these elements in halite are not highly temperature dependent (Valyasko, 1956 and Holser, 1979). The calculated ratios for the Hutchinson Salt and the experimentally observed ratios of evaporated sea water brines are in Table 8.

The calculated ranges of the K/Na (0.161 to 0.608), Ca/Na (0.0002 to 0.058), and Br/Cl (0.0025 to 0.0054) ratios of the brines from which the Hutchinson Salt halite samples precipitated are within the range of values for evaporated sea water brines are reported by Valyasko (1956) and Collins (1975). Each of the calculated ratios, however, indicates a different stage of evaporation of sea water, even within an individual sample. The Br/Cl ratios indicate that the brines were either similar to normal seawater or concentrated to the early stages of halite precipitation, whereas the K/Na ratios suggest a more advanced stage of evaporation. The observed

Table 7. Ionic ratios from halite samples and brine inclusions from the Hutchinson Salt Member of the Wellington Formation.

Sample	Mg/Cl	Ca/Cl	Br/Cl	SO_4/Cl
	Halite Samples (from this study)			
820	0.0009	___	0.000079	0.0023
843	0.0012	0.0154	0.000112	0.0216
880	0.0032	0.0092	0.000173	0.0226
915	0.0004	0.0009	0.000137	0.0036
966	0.0007	0.0058	0.000163	0.0154
1007	0.0007	0.0114	0.000086	0.0224
1036	0.0009	0.0180	0.000106	0.0272
1052	0.0003	0.0122	0.000103	0.0264
1079	0.0013	0.0007	0.000090	0.0026
	Inclusions (from Holser, 1962)			
17167-3	0.2190	___	0.0122	n.d.
17167-4	0.2370	___	0.1380	n.d.
17167-5	0.2470	___	0.0160	0.0340
16947-20	0.2200	___	0.0170	n.d.

Table 8. Comparison of the ionic concentration ratios of the brines that precipitated the halite samples in the Hutchinson Salt Member of the Wellington Formation and of evaporated seawater brines (from Collins, 1975.)

Sample nos.	Br/Cl	K/Na	Ca/Na
	Halite Samples		
820	0.0025	0.161	0.0002
843	0.0035	0.241	0.0530
880	0.0054	0.608	0.0300
915	0.0043	0.188	0.0030
966	0.0051	0.197	0.0200
1007	0.0027	0.227	0.0360
1036	0.0033	0.188	0.0580
1052	0.0032	0.139	0.0350
1079	0.0028	0.309	0.0020
	Sea water brines		
Normal Seawater	0.0034	0.032	0.0360
Gypsum stage	0.0034	0.036	0.0170
Halite stage	0.0145	0.164	0.0007
Epsomite stage	0.0155	0.529	0.0001

elemental ratios of an individual sample cannot be generated either by the progressive evaporation of average seawater or by Raup's (1970 and 1982) model of mixing of various seawater brines. Therefore, the variance must be related either to precipitation of salts from solutions not derived solely from seawater or to post-depositional alteration of salts precipitated from seawater. The former explanation is supported by Sr isotopic data to be presented later.

Anhydrite Samples

The Sr/Ca, Mg/Ca, and K/Ca ratios of the brines from which the pure anhydrite samples precipitated were estimated using experimentally derived values of the distribution coefficients for the trace elements. Kushnir (1980) noted that the distribution coefficients of Sr and Mg are highly temperature dependent whereas that of K is not. Sample no. 971 is excluded from further discussions because it contains too much halite. Considering an estimated temperature range of 40 C to 80 C for the formation of these anhydrite deposits, the Sr x 100/Ca ratio ranges from 3 to 4, the Mg/Ca ratio ranges from 108 to 121, and the K/Ca ratio ranges from 9 to 22. All calculated ratios for the brines from which the anhydrite precipitated are within the range of values for an evaporated seawater brine. However, for the same sample, each calculated ratio indicates a stage of evaporation that is different from stages of evaporation computed from other calculated ratios. Therefore, barring post-depositional alterations, the variance in

the ratios precludes the possibility of the precipitation from progressive evaporation of normal seawater. This variance in the stage of evaporation, however, can be explained on the basis of precipitation from the mixing of brines of seawater origin or the mixing of seawater brines with brines of continental origin.

Dolomite Samples

The major element chemistry of the dolomite samples from the Hutchinson Salt generally is similar to that of other dolomite samples associated with evaporites (Weber, 1964 and Viezer and Demovic, 1974). Figure 11 is a plot of the Mg/Ca ratios versus the Sr/Ca ratios of the dolomite samples from the Hutchinson Salt and several dolomite samples from Viezer and Demovic (1974). The dolomite samples from the Hutchinson Salt are similar to Viezer and Demovics' Group J rocks, which were interpreted as having formed in a hypersaline environment by the replacement of unlithified or partially lithified carbonate muds during sedimentation. By analogy, the dolostone samples from the Hutchinson Salt are considered to have had a similar depositional history.

The conversion of $CaCO_3$ minerals into dolomite by a Mg-rich sea water brine is a popular dolomitization model (Kinsman, 1973 and others). Jones (1965) hypothesized that the dolomite beds in the Hutchinson Salt formed from the alteration of previously deposited $CaCO_3$ minerals by a fluid derived from the evaporation of seawater. Although chemical data from this investigation seem to support Jones' hypothesis, Sr isotopic data to be presented later indicate

that the fluids involved in dolomitization were not entirely of seawater origin.

Using a dolomite-fluid distribution coefficient of 0.35 for Sr, as given by Katz and Matthews (1977), and assuming an open-system-dolomitization process, the Sr/Ca ratio was calculated for the fluid involved in formation of the pure dolomite sample (no. 1220). The other samples contained some small amounts of anhydrite and therefore were not considered in this calculation. The calculated Sr/Ca ratio of the brine with which the dolomite sample was last in equilibrium is about 0.07. This ratio is characteristic of seawater brines approaching halite saturation. Seawater evaporated to halite saturation would have a Li concentration between 10 and 30 ppm and a Mg/Ca ratio between 750 and 8000. A brine of such composition could easily dolomitize limestone (Kinsman, 1973) and in the process enrich the dolomite in Li. In comparison with other evaporitic dolomite samples whose Li contents are generally less than 10 ppm (Weber, 1964), The Li concentration of dolomite sample no. 1220 is 30 ppm. However, any interpretation of these high Li contents in the carbonates should be viewed with caution because significant amounts of Li could be leached from clay minerals which are present in these carbonate rocks.

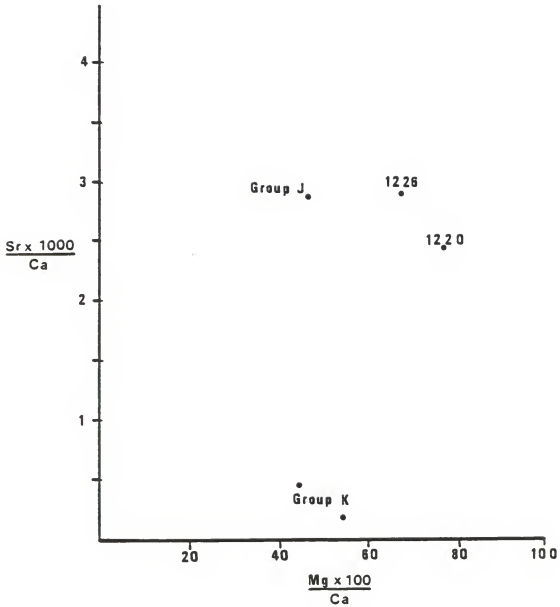


Figure 11. Plot of the Sr/Ca ratios vs. the Mg/Ca ratios of several evaporite associated dolomite samples

DISCUSSION OF Sr ISOTOPIC DATA

The initial $^{87}Sr/^{86}Sr$ ratios of the evaporites in the Hutchinson Salt range from 0.70815 to 0.70897 (Table 3) (Fig. 12). These values are significantly higher than the $^{87}Sr/^{86}Sr$ ratio of about 0.7078 predicted for early Permian seawater by Peterman et al. (1970) and Burke et al. (1982). Because Sr isotopes are not known to fractionate during precipitation from a solution, evaporites will inherit the Sr isotope composition of the brine from which they precipitate. Therefore, the difference in the $^{87}Sr/^{86}Sr$ ratio of Hutchinson Salt evaporite deposit from that of contemporary seawater can be attributed either to post-depositional (i.e. diagenetic) alterations or to differences in the Sr isotopic composition of the brine in the basin at the time of precipitation of the salts. The relative importance of these two processes must be evaluated to account for the observed $^{87}Sr/^{86}Sr$ ratios of the evaporites in the Hutchinson Salt.

Diagenesis

Recrystallization of Halite and Anhydrite--The isotopic variation and the high $^{87}Sr/^{86}Sr$ ratios of the evaporite samples from the Hutchinson Salt could be ascribed to the introduction of Sr from outside the evaporite sequence through the movement of continental groundwaters, which are generally know for their high $^{87}Sr/^{86}Sr$ ratios. Recrystallization of halite in the Hutchinson Salt has been reported by Jones (1965), Dellwig (19962), Swineford (1955), and

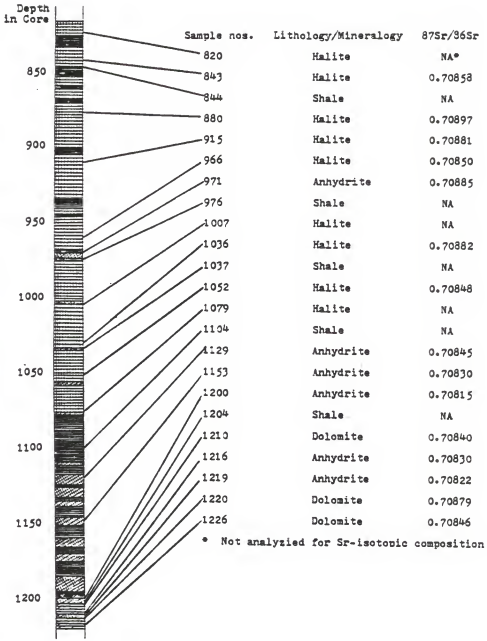


Figure 12. Lithology, location, and $^{87}Sr/^{86}Sr$ ratio of core samples from the Hutchinson Salt Member of the Wellington Formation

Tasch (1964). Although Jones (1965) argued that recrystallization occurred after burial, Dellwig (1962) indicated that recrystallization may have taken place at the bottom of the basin prior to burial. Recrystallization prior to burial would be no significant effect on alteration of the Sr isotopic composition of the halite samples because the fluid promoting recrystallization would have a Sr isotopic composition essentially identical to that of the brine from which the halite samples originally precipitated. Therefore, if recrystallization of the salt occurred prior to burial, the observed $^{87}Sr/^{86}Sr$ ratios of the halite samples indicate that the seawater in the Hutchinson Salt basin at this time must have been enriched in ^{87}Sr relative to contemporary seawater.

Alternatively, the variations in the $^{87}Sr/^{86}Sr$ ratios of the halite and anhydrite samples and their high isotopic values relative to contemporaneous seawater could be the result of post-depositional recrystallization. Any recrystallization model with limited ground water having low Sr and Br contents will not be valid. The volume of fluid needed to change the isotopic composition of the sulfate deposits would have to be very high because of the very high Sr content of the minerals. Large amounts of fluid with low Br contents will undoubtedly lower the Br contents of the halite deposits to values significantly below the range of values for typically marine halite deposits. Because the Br contents of the halite minerals in the Hutchinson Salt are within the range of values for marine deposits, the isotopic compositions of the anhydrite and halite samples cannot be explained by post-depositional recrystallization in the presence of low Sr- and

Br-bearing waters, which are characteristic of shallow, chemically less evolved ground water. A possibility exists that recrystallization of both halite and anhydrite samples occurred in the presence of highly chemically evolved ground waters with high Sr and Br contents and High $^{87}Sr/^{86}Sr$ ratios. In this context of recrystallization, any simple two component mixing is not apparent from Sr isotopic data and the Sr contents of the halite samples. Also, the Sr/Ca ratios of the halite samples do not bear any predictable trend with their $^{87}Sr/^{86}Sr$ ratios. For instance, halite samples no. 915 and no. 1036 have identical Sr isotopic ratios of 0.70881, yet one has a Sr/Ca of 0.30 while the other has a ratio of 0.01.

Although the isotopic data do not totally negate recrystallization as one mechanism by which the salts could have inherited the observed isotopic characteristics, the same array of data can also be considered as signatures of primary isotopic values. The model proposed to account for the high $^{87}Sr/^{86}Sr$ ratios of both halite and anhydrite samples from the Hutchinson Salt evaporite sequence entails a mixing of varied evaporated seawater and continental water that was enriched in ^{87}Sr.

Dolomitization--Petrographic studies by Jones (1965) and others have shown that the dolomite in the Hutchinson Salt was formed by the diagenetic replacement of the originally deposited carbonate minerals. Jones (1965) also suggested that the carbonate minerals n the Hutchinson Salt were dolomitized by an evaporated seawater brine. Chemical data from the present investigation support this

hypothesis. The approximate time of replacement, estimated by comparison of Sr/Ca ratios as proposed by Veizer and Demovic (1974), indicates that dolomitization occurred shortly after burial of the original carbonate sediments.

In the preceding discussing on chemical analysis I have argued that the brines with which the dolomite samples were last in equilibrium had Li contents and Sr/Ca ratios similar to those of seawater evaporated to near halite saturation. Therefore, the fluid involved in dolomitization of the carbonates in the Hutchinson Salt may have been derived from an evaporated seawater brine that was entrapped in the halite beds during their deposition. These brines would have an $^{87}Sr/^{86}Sr$ ratio in the range of 0.70848 to 0.70897 (i.e. the measured range of the halite samples). The introduction of such brines into carbonates, whose original $^{87}Sr/^{86}Sr$ ratios were similar to that of contemporary sea water, could be accounted for the observed $^{87}Sr/^{86}Sr$ ratio of the dolomite samples. The ratio of 0.70879 is within the range of ratios for the halite samples. The other two dolomite samples contain trace amounts of anhydrite and therefore, the relatively low ratios of these two samples may be artifacts of sample inhomogeneity.

Alternatively, because the dolomite samples have relatively high insoluble residue contents, the high $^{86}Sr/^{86}Sr$ ratios of the dolomite samples could be related to the introduction of Sr from clay minerals either during diagenesis or through leaching during laboratory dissolution. Clay minerals are known to be enriched in Sr and also have very high Li contents. Present data are insufficient to determine which of these two processes is

responsible for the high Sr isotopic ratios and Li contents of the dolomite samples.

Chemical Evolution of the Hutchinson Salt Brines

The preceding discussion has argued in favor of the hypothesis that the Sr isotopic compositions of the anhydrite and halite samples from the Hutchinson Salt may truly reflect the Sr isotopic composition of the saline water from which the evaporites precipitated. Because the Hutchinson Salt evaporites formed in a restricted marine basin and their observed $^{87}Sr/^{86}Sr$ ratios are higher than that of contemporaneous seawater, the high isotopic ratios of the evaporites must be related to an influx of Sr that was enriched in ^{97}Sr into the basin prior to the deposition of these evaporites.

Raup (1970 and 1982) proposed that evaporites may be deposited as a result of the mixing of brines of various concentrations and Clauer (1976) has found the $^{87}Sr/^{86}Sr$ ratio of Miocene evaporites to be less than that of the contemporary seawater, a fact he attributes to the influx of continental waters depleted in ^{97}Sr into the evaporating basin. The mixing in varying proportions between contemporaneous Permian sea water and continental brines that were enriched in ^{87}Sr relative to the seawater, could have generated, under certain circumstances, saline waters with Sr isotopic composition that were similar to the values observed in halite and anhydrite samples of the Hutchinson Salt evaporites.

The extent to which the Sr isotope composition of a marine water

in a restricted basin is affected by an influx of continental water is dependent on (1) the amount of continental influx, (2) the Sr contents and $^{87}Sr/^{86}Sr$ ratios of the continental waters, and (3) the stage or extent of evaporation of the seawater in the basin. A series of calculations were carried out to estimate the amount and Sr isotopic composition of an influx of continental waters necessary to generate a brine in an evaporating seawater basin whose Sr isotopic composition is similar to that of the halite samples from the Hutchinson Salt (Table 9). The equations used in these calculations are as follows:

$$(Sr)m = (f)\ (Sr)sw + (1-f)\ (Sr)cw$$

$$(Sr)m\ (r)m = (f)\ (Sr)sw\ (R)sw + (1-f)\ (Sr)ce\ (R)cw$$

Where, m = mixed water brine

sw = seawater

cw = continental water

Sr = Sr concentration (in ppm)

R = $^{87}Sr/^{86}Sr$ ratio

f = fraction of seawater

Table 9. Comparison of the mixing of seawater and continental brines.

(Sr)sw	(R)sw	(Sr)cw	(R)cw	(1-f)	(Sr)m	(R)m
10	0.7078	100	0.7280	0.01	10.9	0.7097
10	0.7078	100	0.7280	0.05	14.5	0.7148
10	0.7078	10	0.7280	0.01	10.0	0.7079
10	0.7078	10	0.7280	0.05	10.0	0.7088
10	0.7078	10	0.7280	0.10	10.0	0.7099
10	0.7078	10	0.7350	0.01	10.0	0.7081
10	0.7078	10	0.7350	0.05	10.0	0.7091
10	0.7078	100	0.7200	0.01	10.9	0.7089
10	0.7078	100	0.7200	0.05	14.5	0.7121

The calculations reveal that the influx of a relatively small amount (1% to 5%) of continental water with both high Sr contents (10 to 100 ppm) and high $^{87}Sr/^{86}Sr$ ratio (0.7200 to 0.7350) could generate a brine whose Sr isotopic composition would be similar to that of the halite samples from the Hutchinson Salt. Due to the complexities associated with the dehydration of gypsum to anhydrite, estimation of the chemical composition of the evaporated sea water brine from which the sulfates precipitated was not attempted.

The evaporite sequence of the Hutchinson Salt Member is interlayered with then beds of shale. Figure 13 presents the $^{87}Sr/^{86}Sr$ ratios of the evaporite samples and their relationship to the interbedded shale layers. The presence of these shale beds in the evaporite sequence indicates that during the deposition of the evaporite sequence the basin received periodic influx of surficial continental waters and that at these times clastic deposition dominated over evaporite deposition (Tasch, 1964). The influx of an average surface water into the Hutchinson Salt basin would not have been sufficient to bring about measurable alterations in the Sr isotopic composition of the brine in the evaporating basin unless the $^{87}Sr/^{86}Sr$ ratios of the influxing waters were very high.

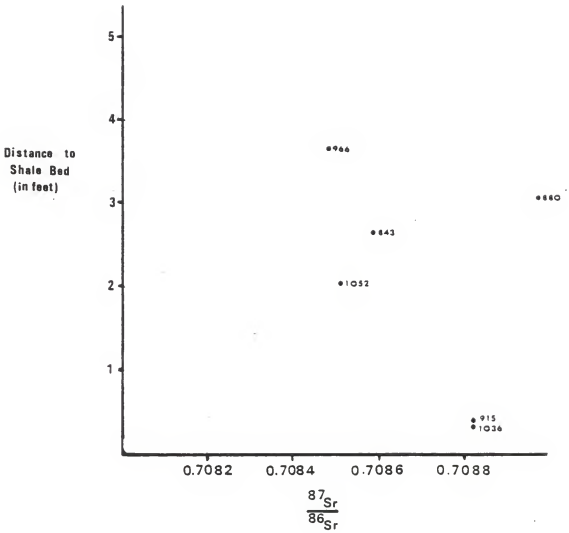


Figure 13. Plot of the $^{87}Sr/^{86}Sr$ ratios vs. the distance to a shale bed of halite samples from the Hutchinson Salt Member of the Wellington Formation

Considering the geologic setting of the Hutchinson Salt Basin, The Sr isotopic composition of any surface runoff was possible influenced by that of the Paleozoic carbonate rocks of the surrounding land mass, whose $^{87}Sr/^{86}Sr$ ratios were 0.70900 or less. Because of the generally low Sr contents of about 0.07 ppm (Wadleigh et al., 1985) and apparently low $^{87}Sr/^{86}Sr$ ratios of these surficial waters, any measurable alteration of the Sr isotopic composition of the brine in the basin would have required an extremely large influx of surficial continental waters. For example, 50 percent of a highly enriched seawater brine with Sr contents of about 5 ppm and an $^{87}Sr/^{86}Sr$ ratio of about 0.7078 mixed with continental water with 0.07 ppm Sr and an $^{87}Sr/^{86}Sr$ ratio of about 0.7100 produces a change no greater than 3 parts in 70,000. The influx of a large volume of fresh surface water into an evaporating basin would eventually prevent the precipitation of evaporites. Therefore, alteration of the Sr isotopic composition of the brine in the Hutchinson Salt basin by an influx of surficial continental runoff seems unlikely. Table 10 presents the elemental concentrations of several continental and marine brines. The continental brines often have high $^{87}Sr/^{86}Sr$ ratios and Sr contents.

Table 10. Elemental concentrations (in ppm) of several evaporated seawater brines and of subsurface brines (from Collins, 1975).

	K	Na	Ca	Mg	Sr	Cl	Br	SO_4
				Seawater				
seawater	350	11000	400	1300	7	19000	65	___
$CaSO_4$	3600	98000	1700	13000	60	178000	600	___
$NaCl^4$	23000	140000	100	74000	10	275000	4000	___
KCl	26000	13000	0	130000	0	360000	8600	___
Miss.	430	41500	8900	1600	630	85000	410	540
Penn.	170	43000	9100	1900	600	87600	490	430
Permian	170	47000	8600	2000	7	92700	46	730
Jurassic	140	57300	25800	2500	320	141000	1200	210

Thus, the influx of a saline continental water with a Sr concentration greater than seawater would have a much greater effect on the Sr isotope composition of an evaporating seawater brine than would the influx of a similar volume of fresh water with a Sr content much lower than that of seawater.

The alteration of the $^{87}Sr/^{86}Sr$ ratio of a marine brine without the influx of a large volume of continental water could be accomplished if the continental waters had high Sr contents or high $^{87}Sr/^{86}Sr$ ratios or both. Studies have shown many subsurface formation waters to be enriched in both Sr contents and ^{87}Sr. These waters, whose salinity may be as much as 10 times that of normal seawater, are often classified as Na-Ca-Cl type waters. Therefore, an introduction of a small amount of this type of continental water would not alter the major chemical composition of the brine in the evaporating basin to the extent that the precipitation of evaporite minerals would cease.

Chaudhuri (1978) has reported $^{87}Sr/^{86}Sr$ ratios as high as 0.7350 and Sr concentrations of 100 ppm and above in some formation waters in Paleozoic rocks. Because these $^{87}Sr/^{86}Sr$ ratios and Sr contents are much higher than those of seawater, a small influx of such waters could measurably alter the Sr isotopic composition of the brine in the basin. The high values of the $^{87}Sr/^{86}Sr$ ratios of the evaporites from the Hutchinson Salt relative to contemporary seawater could be explained by such an influx. Furthermore, the influx of saline continental waters could also have accounted for the previously noted differences in the stage of seawater evaporation as determined from different chemical parameters within

a single sample and for the advanced concentration of brine inclusions in halite samples from the Hutchinson Salt noted by Holser (1962).

The influence of an influx of continental water can also be critically examined through analysis of the $^{87}Sr/^{86}Sr$ ratios of the halite samples and their relative stages of precipitation. The Sr concentration of sea water progressively changes with evaporation, first increasing from 8 ppm to a high value of 60 ppm (prior to gypsum precipitation) followed by a gradual decrease to less than 10 ppm (after precipitation of halite) and then to less than 1 ppm (after precipitation of sylvite). Thus, the influence of an influx of continental water enriched in ^{87}Sr will be most pronounced at later stages of evaporation, such as that of halite, should be greater than those formed at an earlier stage of evaporation, such as sulfates. The observed $^{87}Sr/^{86}Sr$ ratios of halite samples (0.70848 to 0.70897) from the Hutchinson Salt are higher than those of the anhydrite samples (0.70815 to 0.70845). This trend is in agreement with the proposed model of mixing between seawater brines and continental waters enriched in ^{87}Sr.

Valyasko (1956) showed that Br/Cl ratios of evaporated seawater increase during progressive stages of evaporation. The calculated Br/Cl ratios for the brine from which the halite samples precipitated range from 0.0032 in sample 1052 to 0.0051 in sample no. 880, therefore sample no. 880 represents the halite sample precipitated from the most concentrated brine. The most concentrated brine resulting from the most advanced stage of evaporation will have relatively low Sr contents. At this time,

influx of Sr from a continental source have a High $^{87}Sr/^{86}Sr$ ratio and high Sr content would have a maximum effect on increasing the $^{87}Sr/^{86}Sr$ ratio of the brine in the basin. Sample no.880 has the highest observed Br/Cl ratio and also has the highest $^{87}Sr/^{86}Sr$ ratio among the samples analyzed. Similarly, the samples with lower Br/Cl ratios, indicating precipitation from a less advanced stage of evaporation of seawater, should have lower $^{87}Sr/^{86}Sr$ ratios. The high Sr contents of the brine at this stage of evaporation will tend to temper to a greater degree the influence of any continental influx. In view of this sample no. 1052 with a low Br/Cl ratio and low $^{87}Sr/^{86}Sr$ ratio probably precipitated from a brine at a lesser stage of evaporation than the brine from which sample no. 880 precipitated. Although this inverse relationship between the $^{87}Sr/^{86}Sr$ and Br/Cl ratios is not valid for all of the halite samples, it does appear that the observed variations in the $^{87}Sr/^{86}Sr$ ratios of the halite samples may have been effected by the mixing of highly saline continental water with evaporated marine brines at different stages of evaporation prior to the precipitation of the halite samples.

DISCUSSION OF Pb-Cu-Zn DATA

Analyses of shale samples from the Hutchinson Salt evaporite deposit reveal that the absolute concentrations of Pb, Cu, and Zn are greater in the shale samples associated with anhydrite beds than in the samples from the halite beds (Table 4). However, the Pb/Cu, Pb/Zn, and Cu/Zn ratios of all shale samples are very similar (Table 10). Because clay mineral analysis has shown all shale beds to contain similar clay minerals, the observed difference between the absolute concentrations of the metals in these various shale samples is probably related to different amounts of the metal-bearing mineralogic phases in the shale beds.

The range of Cu concentration (0.14 to 0.54 ppm) of the halite samples from the Hutchinson Salt is well within the range of 0.09 to 6.50 ppm of Cu in halite samples from other geographic locations, such as the Elk Point evaporite sequence of Canada, the Zechstein evaporite sequence of Germany, and the Hermosa Formation of the southwestern United States (Theide and Cameron, 197888) (Table 11). The Zn concentrations of the halite samples from the Hutchinson Salt (range 2.3 to 9.0 ppm) are much higher than the range of 0.1 to 1.2 ppm found in the halite from other geographic locations. Because of the lack of data on the behavior of these elements in halite, specifically distribution coefficients, it is not possible at this time to theorize on the processes responsible for the relatively high Zn concentrations in the halite samples from the Hutchinson Salt.

Table 11. Pb/Cu, Pb/Zn, and Cu/Zn ratios of shale samples from the Hutchinson Salt Member of the Wellington Formation.

Sample no.	Pb/Cu	Pb/Zn	Cu/Zn
844	0.096	0.016	0.167
976	0.016	0.017	1.057
1037	0.014	0.007	0.523
1104	___	___	0.133
1204	0.017	0.008	0.500

Table 12. Metal contents of halite and shale samples from the Elk Point Group (Saskatchewan) and the Hermosa Formation (Utah) (from Theide and Cameron, 1978).

Sample	lithology	Pb	Cu	Zn
	Elk Point Group			
___	rock salt	0.30	0.30	1.10
___	red shale	22.90	12.70	29.00
___	green shale	45.10	22.30	22.60
	Hermosa Formation (Paradox Member)			
___	black shale	3.70	46.00	21.00
___	rock salt	1.10	2.30	0.12
___	rock salt	1.20	6.50	0.56

SUMMARY

1. The $^{87}Sr/^{86}Sr$ ratios of all of the evaporite samples from the Lower Permian Hutchinson Salt member are enriched in ^{87}Sr relative to contemporaneous Permian marine Sr.

2. The halite samples, whose $^{87}Sr/^{86}Sr$ ranged from 0.70848 to 0.70897, have the greatest enrichment in ^{87}Sr, whereas the anhydrite samples, whose $^{87}Sr/^{86}Sr$ ranged from 0.70815 to 0.708885, have a lesser enrichment in ^{87}Sr.

3. Analysis of Br and Sr_4 contents indicate that the high$^{87}Sr/^{86}Sr$ ratios of the halite and anhydrite samples relative to the contemporaneous seawater isotopic value were not necessarily caused by diagenetic alteration.

4. The high $^{87}r/^{86}Sr$ ratios of the halite and anhydrite samples can be attributed to an enrichment in ^{87}Sr of the brine in the Hutchinson Salt basin prior to the deposition of the evaporites.

5. The shale beds within the evaporite sequence indicates that significant influx of surficial continental water periodically occurred during evaporite deposition. However, because of the generally low Sr contents (<0.1 ppm) and apparently low $^{87}Sr/^{86}Sr$ ratios (<0.709) of these waters, significant alteration of the $^{87}Sr/^{86}Sr$ ratio of the brine in the Hutchinson Salt Basin would

require such a large volume of fresh water as to prohibit evaporite deposition.

6. It is proposed that the enrichment in ^{87}Sr of an evaporated seawater brine at various stages of evaporite deposition in the Hutchinson Salt basin and the resultant variations in the $^{87}Sr/^{86}Sr$ ratios of the evaporite samples could be related to the periodic influx of subsurface, continental brines with high $^{87}Sr/^{86}Sr$ ratios.

7. Shale from the Hutchinson Salt Member were enriched in Cu (23 to 858 ppm) and in Zn (172 to 1700 ppm) and depleted in Pb (5 to 14 ppm) compared to an average shale.

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Chemical and Sr Isotope Investigations of the Lower Permian Hutchinson Salt Member of the Wellington Formation, Rice County, Kansas

by

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ABSTRACT

Twenty-three samples from the Hutchinson Salt Member of the Wellington Formation (9 halite, 6 anhydrite, 3 dolomite, and 5 shale samples) were collected from the core of the Atomic Energy Commission's Test Hole no. 1 in Rice County, Kansas. The evaporite samples were analyzed for their major element, trace element, and Sr isotope compositions. The results of the major-element analyses generally agree with other analyses of similar evaporitic sequences. Trace-elemental analyses revealed that the dolomite samples are somewhat enriched in Li (30 ppm) in comparison to other evaporite associated dolomite samples may be the result of dolomitization of the originally deposited CaCO3 minerals by a highly-saline, seawater-derived brine originating within the salt sequence and passing through the carbonates upon compaction of the halitic sediments.

The $^{87}Sr/^{86}Sr$ ratios of the samples (range 0.70815 to 0.70895) are all higher than the value of 0.70750 predicted by Petermann et al. (1970) for Early Permian seawater. The greatest enrichment is in the halite samples (range 0.70848 to 0.70897) and in the pure dolomite sample (0.70875). The ratios of the anhydrite samples ranged from 0.70815 to 0.70845. The enrichment in the $^{87}Sr/^{86}Sr$ ratios of the evaporite samples is attributed to the influence of continental waters on the Sr-isotopic composition of the water in the Hutchinson Salt basin.

Five shale samples were found to contain illite, cholorite, and a

mixed-layer clay mineral thought to be corrensite. The Pb, Cu, and Zn contents of the shale samples and the Cu, and Zn compositions of the halite samples were determined, and it was found that the shale samples are enriched in Cu (22.9 to 854.8 ppm) and Zn (172 to 1709 ppm) but are somewhat depleted in Pb (4.6 to 14.2 ppm) as compared to an average shale. No relationship was evident between the metal contents of the shale beds and their clay minerals.